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Key Points:

- A new semiempirical approach is developed for obtaining total atmospheric lifetimes of halocarbons from their photochemical properties
- The new approach yields partial lifetimes for methyl chloroform of 6.0 years for OH reaction and 48 years for stratospheric photolysis
- The methyl chloroform scaling approach is shown to yield total (rather than tropospheric) lifetime estimates for long-lived halocarbons

Supporting Information:

- Supporting Information S1

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Atmospheric Lifetimes of Halogenated Hydrocarbons: Improved Estimations From an Analysis of Modeling Results

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Abstract Detailed results of computer modeling of halocarbon removal rates from the atmosphere are analyzed to find simple correlations useful for improving estimations of the atmospheric lifetimes of industrial chemicals based on the rate constants for their reactions with OH and O(¹D) and their UV absorption spectra. This analysis is limited to relatively long-lived chemicals that are well mixed in the troposphere.

1. Introduction: Atmospheric Lifetime Determination

The chemical composition of the Earth's atmosphere has been an area of general research interest for decades (Levy, 1971). A number of environmental issues have fostered detailed quantitative studies. These include such topics as (i) the destruction of stratospheric ozone via photochemical cycles involving Cl- and Br-containing industrial halocarbons and their reaction products (WMO, 2018), (ii) the alteration of the radiative balance of the Earth's atmosphere due to the buildup of infrared absorbing gases and other constituents in the upper troposphere and lower stratosphere (IPCC, 2001), and (iii) the production and transport of ozone and other pollutants in the troposphere (Atkinson, 2000; Chameides & Walker, 1973; Crutzen, 1973, 1974; Haagen-Smit, 1952; Thompson, 1992). Inherent in such quantification are the residence times in the atmosphere of the applicable source gases and the rates of the initial steps in their atmospheric degradation. Reactions with hydroxyl radicals (OH) in the troposphere dictate the atmospheric residence times of the majority of industrial and natural compounds. Whereas substantial progress has been achieved in accurate laboratory measurements of the rate constants for the reaction between an atmospheric trace gas and OH, estimation of a compound's total atmospheric lifetime involves some uncertainties due to the heterogeneity of the atmosphere including the slow vertical mixing of the stratosphere.

The total lifetime of a trace compound in the atmosphere is defined as the ratio of its global atmospheric burden (C_{global}) to its total atmospheric removal rate (L_{total})

$$\tau_{total} = C_{global}/L_{total}, \quad (1)$$

L_{total} can be expressed as the sum of the loss rates for various removal processes in the atmosphere (gas-phase reactions and photolysis) and loss rates due to dissolution in the ocean, soil uptake, and other minor removal processes.

$$L_{total} = L_{atm} + L_{ocean} + L_{soil} + L_{other}. \quad (2)$$

Atmospheric loss rates, L_{atm} , which will be considered in this paper, can be separated into three different loss regions (troposphere, stratosphere, and mesosphere), each of which are characterized by different physical properties, with different mixing time scales being the most important. Loss processes in the very low density conditions of the mesosphere (mainly photolysis at 121.6 nm, Lyman- α wavelength) have generally negligible contributions to L_{atm} ; they are important only for extremely long-lived per-fluorinated compounds, which undergo neither chemical reaction in the atmosphere nor UV photolysis in the stratosphere. Thus,

$$\frac{1}{\tau_{atm}} = \frac{L_{atm}}{C_{global}} = \frac{L_{trop} + L_{strat} + L_{meso}}{C_{trop} + C_{strat} + C_{meso}} \cong \frac{L_{trop} + L_{strat}}{C_{trop} + C_{strat}}. \quad (3)$$

Global chemistry model estimates of the lifetimes of hydrogen containing compounds such as HFCs and HCFCs (which are primarily removed due to reactions with OH) can be subject to large uncertainties. These uncertainties stem primarily from the difficulty in estimating the absolute abundance of OH in the atmosphere, which has very large spatial and temporal variability over the globe. Methyl chloroform (MCF, CH_3CCl_3), an atmospheric trace gas of purely industrial origin with well known emission inventories, is primarily removed from the atmosphere via its reaction with OH and has been used to infer the global OH abundance. Moreover, since the production and use of MCF was banned, the decay of its atmospheric concentration during last two decades has been driven mainly by removal processes with much lower or essentially no emission. Thus, earlier uncertainties in its emission rate probably had only a small effect on its lifetime estimations. The total atmospheric lifetime of MCF, τ_{MCF} , has been estimated from an analysis of its atmospheric concentration and trend without the need for photochemical modeling of atmosphere (Prinn et al., 2005; Rigby et al., 2013). This empirically determined lifetime has then been used in a simple scaling procedure to estimate the tropospheric lifetimes of other hydrogen containing trace gases (RH_i) that are also removed from the atmosphere primarily via their reactions with OH (Prather & Spivakovsky, 1990; Spivakovsky et al., 2000)

$$\tau_{\text{RH}_i}^{\text{OH}} = \frac{k_{\text{MCF}}(272 \text{ K})}{k_{\text{RH}_i}(272 \text{ K})} \tau_{\text{MCF}}^{\text{OH}}, \quad (4)$$

where $\tau_{\text{RH}_i}^{\text{OH}}$ and $\tau_{\text{MCF}}^{\text{OH}}$ are the lifetimes of a target compound and methyl chloroform, respectively, due to their reactions with hydroxyl radicals in the troposphere only, and $k_{\text{RH}_i}(272 \text{ K})$ and $k_{\text{MCF}}(272 \text{ K})$ are the rate constants for the reactions of OH with these substances at $T = 272 \text{ K}$ (Burkholder et al., 2015). The temperature, $T = 272 \text{ K}$, was found to be the most appropriate single temperature for such scaling when the Arrhenius activation energies, E/R , of the OH reaction rate constants, range from 0 to 2,500 K, although $T = 270 \text{ K}$ can be used for temperature independent rate constants (Spivakovsky et al., 2000). This scaling procedure effectively establishes a “pseudo” tropospheric OH climatology responsible for the tropospheric removal of MCF. Thus, the best scaling temperature is dependent on a model’s OH distribution. The value of the MCF partial lifetime due to its reaction with OH in the troposphere, $\tau_{\text{MCF}}^{\text{OH}}$, for use in expression (4) can be obtained from the total lifetime of MCF derived from field measurements of its concentration, τ_{MCF} , after oceanic and stratospheric losses are taken into account

$$\left(\tau_{\text{MCF}}^{\text{OH}}\right)^{-1} = \left(\tau_{\text{MCF}}\right)^{-1} - \left(\tau_{\text{MCF}}^{\text{strat}}\right)^{-1} - \left(\tau_{\text{MCF}}^{\text{ocean}}\right)^{-1}. \quad (5)$$

It is assumed that the value for $\tau_{\text{RH}_i}^{\text{OH}}$ derived from (4) is the partial lifetime of a compound due to its reaction with OH in the troposphere, $\tau_{\text{trop}}^{\text{OH}}$, whereas the total lifetime is needed to characterize the atmospheric pollutant and estimate its global impact indices such as ODP or GWP. Therefore, by analogy with Equation 5 and in the absence of oceanic loss, $\tau_{\text{RH}_i}^{\text{OH}}$ is typically combined with the partial lifetimes associated with stratospheric removal processes to derive the total lifetime:

$$\left(\tau_{\text{RH}_i}\right)^{-1} = \left(\tau_{\text{RH}_i}^{\text{OH}}\right)^{-1} + \left(\tau_{\text{RH}_i}^{\text{strat}}\right)^{-1}, \quad (6)$$

where the stratospheric removal rate is assumed to be a sum of removal rates of various stratospheric processes such as the reactions with OH radicals and $\text{O}(^1\text{D})$ atoms in the stratosphere and photolysis by UV radiation near 200 nm penetrating the stratosphere.

$$\left(\tau_{\text{RH}_i}^{\text{strat}}\right)^{-1} = \left(\tau_{\text{strat}}^{\text{OH}}\right)^{-1} + \left(\tau_{\text{strat}}^{\text{ph}}\right)^{-1} + \left(\tau_{\text{strat}}^{\text{O}^1\text{D}}\right)^{-1}. \quad (7)$$

Note that these partial removal rates can be coadded to derive the total stratospheric removal rate (7) only if the corresponding processes in the stratosphere are independent.

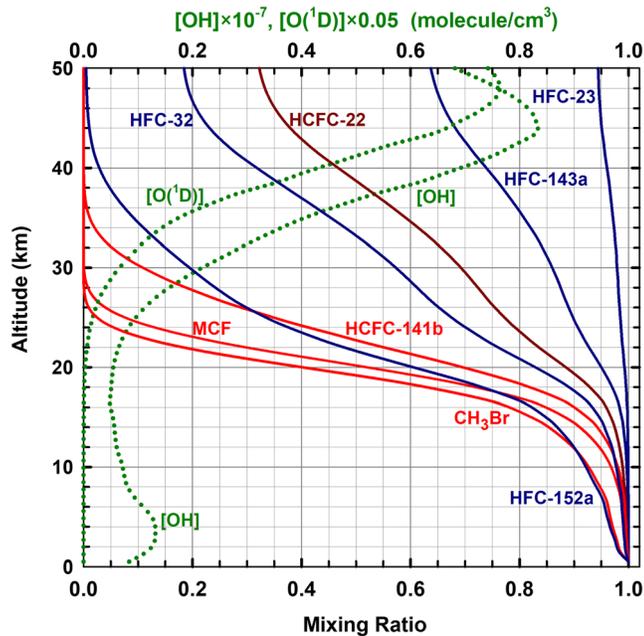


Figure 1. Model-derived global annual averaged altitudinal profiles of atmospheric trace gases and reactive components. Mixing ratios normalized by the ground level values are shown with solid lines: red for stronger UV absorbers (CH_3Br , CH_3CCl_3 , and CH_3CFCl_2), dark red for a weak UV absorber (CHF_2Cl), and blue for nonabsorbing compounds (CH_3CHF_2 , CH_2F_2 , CH_3CF_3 , and CHF_3). Absolute concentrations of OH and $\text{O}(^1\text{D})$ are shown with green dotted lines.

As we noted in earlier papers (Orkin & Khamaganov, 1993; Orkin et al., 1996), although the effect of including the stratospheric removal processes is small, it requires further discussion as illustrated by the following simplified example. In particular, the difference between the altitudinal distributions of methyl chloroform (the reference compound) and the compound of interest in the stratosphere needs to be taken into account. Due to its very strong absorption of UV radiation near 200 nm, MCF is nearly completely photolyzed in the lower stratosphere and, hence, its abundance does not extend to higher altitudes where it could react with stratospheric OH and $\text{O}(^1\text{D})$ as illustrated in Figure 1, i.e., in case of MCF $C_{\text{global}} \cong C_{\text{trop}}$. As a result, the reaction with OH in the troposphere is essentially the total reactive removal channel for MCF in the entire atmosphere and its total lifetime due to photochemical removal in the entire atmosphere ($\tau_{\text{MCF}}^{\text{total}}$) can be approximated as

$$\frac{1}{\tau_{\text{MCF}}^{\text{total}}} = \frac{L_{\text{trop}} + L_{\text{strat}}}{C_{\text{global}}} \cong \frac{L_{\text{trop}} + L_{\text{strat}}}{C_{\text{trop}}} \cong \frac{1}{\tau_{\text{MCF}}^{\text{OH}}} + \frac{1}{\tau_{\text{strat}}^{\text{ph}}}. \quad (8)$$

A similar correlation between $\tau_{\text{RH}_1}^{\text{OH}}$ derived from the Equation 4 and the total lifetime of a compound, $\tau_{\text{RH}_1}^{\text{total}}$, can be expected for other strong UV absorbers like $-\text{CCl}_3$, $-\text{CCl}_2$, $-\text{CBr}$ containing compounds. In contrast, stratospheric profiles of weak or non-UV absorbing compounds (e.g., HFCs) are significantly different from that of MCF resulting in larger fraction of such compounds available in the stratosphere (see Figure 1). The total lifetime of such nonabsorbing compound can be estimated as

$$\frac{1}{\tau_{\text{HFC}}^{\text{total}}} = \frac{L_{\text{trop}} + L_{\text{strat}}}{C_{\text{trop}} + \Delta C_{\text{strat}}} = \frac{\frac{L_{\text{trop}}}{C_{\text{trop}}}}{1 + \frac{\Delta C_{\text{strat}}}{C_{\text{trop}}}} + \frac{L_{\text{strat}}}{C_{\text{trop}} + \Delta C_{\text{strat}}} = \frac{\frac{1}{\tau_{\text{HFC}}^{\text{OH}}}}{1 + \frac{\Delta C_{\text{strat}}}{C_{\text{trop}}}} + \frac{1}{\tau_{\text{HFC}}^{\text{strat}}}, \quad (9)$$

where ΔC_{strat} is the stratospheric abundance of a compound, which is very small in case of MCF and other strong UV absorbers. A comparison of expressions (9) and (8) illustrates that the correction required for estimating the total lifetime based on $\tau_{\text{HFC}}^{\text{OH}}$ is not easily quantifiable because the additional amount of a compound in the stratosphere increases the total lifetime, whereas additional loss due to reactions of the compound in the stratosphere decreases it. Thus, in contrast with strong UV absorbers, it is not immediately obvious which lifetime, $\tau_{\text{HFC}}^{\text{OH}}$ or $\tau_{\text{HFC}}^{\text{total}}$, is longer. In the case of HFCs and weakly absorbing HCFCs, these two corrections offset and Equation 4 may actually yield a good approximation of the total atmospheric lifetime. However, this could not be verified without rigorous mathematical modeling of photochemical processes in the slowly (vertical) mixing stratosphere with nonuniform altitudinal distributions of reactants and UV radiation intensity.

2. Stratospheric Removal Processes and their Partial Lifetimes

Modeling performed by several research groups for SPARC Report No. 6 “Lifetimes of Stratospheric Ozone Depleting Substances, Their Replacements, and Related Species” (SPARC, 2013) provided total lifetimes for a number of compounds as well as their partial lifetimes due to specific photochemical removal processes (reactions with OH in the troposphere, reactions with OH in the stratosphere, reactions with $\text{O}(^1\text{D})$, and photolysis), and partial lifetimes associated with the atmospheric removal regions (troposphere and stratosphere). We have analyzed these results in an effort to find correlations useful for estimating the lifetimes of other atmospheric trace gases based only on laboratory data of their photochemical properties.

Unfortunately, only two of the modeling groups studied the majority of compounds presented in the SPARC Report, including HFCs (2-D model and 3-D model from NASA Goddard Space Flight Center, designated in

the SPARC Report as GSFC2D and GEOSCCM, respectively). Although we performed analyses for all available data, we will primarily show the results of our analysis of the data obtained by the GSFC2D model, the only model which used the most updated kinetic input data for calculating partial lifetimes and studied all compounds listed in the SPARC Report. The detailed results obtained with this model are listed in the Supporting Information.

In this paper we discuss the results of model-calculated loss rates of trace gases in both the troposphere and stratosphere due to initial photochemical steps:

1. stratospheric reactive losses to check for a correlation between τ_{strat}^{OH} and $\tau_{RH_i}^{OH}$ and recommend a semiempirical expression for both τ_{strat}^{OH} and $\tau_{strat}^{O(^1D)}$;
2. stratospheric photolysis loss to recommend a semiempirical expression for τ_{strat}^{ph} ;
3. combined loss rate due to different processes in the slow vertical mixing stratosphere.

Based on this analysis, we suggest an improved semiempirical approach for deriving a “best” value of the total atmospheric lifetime due to photochemical removal processes, $\tau_{RH_i}^{total}$, based on laboratory-derived photochemical properties of a compound, which is consistent with both the empirically derived tropospheric lifetime of MCF and results of rigorous atmospheric modeling.

2.1. Stratospheric Reactive Loss Rates

The majority of hydrogen containing compounds are removed from the atmosphere via their reactions with OH in both the troposphere and stratosphere, which dictates their atmospheric lifetimes. However, for certain classes of hydrogen containing compounds (e.g., HFCs) stratospheric removal by reactions with O(¹D) atoms are also important. Although the stratospheric concentrations of OH and O(¹D) are related to each other through a series of chemical reactions, their altitudinal distributions are different (see Figure 1). In particular, the concentration of O(¹D) increases more rapidly with altitude in the lower stratosphere than that of OH and reactions with O(¹D) in the upper stratosphere can be significant loss processes. Because the concentration of O(¹D) is quite small in the troposphere and lower stratosphere, its reactions contribute only to the lifetimes of compounds that can reach the upper stratosphere. Because OH reactions are the dominant atmospheric loss processes even for slow reacting HFCs (with a lesser contribution due to O(¹D) reactions at higher altitudes), one might expect a correlation between an HFC's stratospheric lifetime and its total lifetime.

Figure 2 shows partial stratospheric “reactive” lifetimes (including both OH and O(¹D) reactive removal processes) for modeled HFCs (compounds with no UV absorption) versus their modeled total atmospheric lifetimes obtained in GSFC2D (2-D model). Fluorinated hydrocarbons listed in the order of increasing lifetimes are HFC-152a (CH₃CHF₂), HCF-32 (CH₂F₂), HFC-245fa (CHF₂CH₂CF₃), HFC-134a (CH₂FCF₃), HFC-125 (CHF₂CF₃), HFC-227ea (CF₃CHFCF₃), and HCF-23 (CHF₃). As can be seen, there is a good linear correlation between total and stratospheric reactive lifetimes for all compounds except HFC-143a (CH₃CF₃) and methane, which are shown with open circles and were not used in deriving the correlation. Thus, we derive a linear dependence between stratospheric lifetimes of HFCs and their total lifetimes spanning between 1.5 and 230 years:

$$\log(\tau_{strat}^n) = 1.521 + 0.8306 \times \log(\tau_{total}). \quad (10)$$

Figure 2 also shows (open squares) partial lifetime due to reactions with OH only in the stratosphere, τ_{strat}^{OH} , i.e., not including O(¹D) reaction loss. Thus, Figure 2 illustrates that the reactions with OH are the dominant removal processes for all studied compounds except HFC-143a, methane, and, to the lesser extent, HFC-23. We can derive a dependence similar to (10) for the partial lifetime due to only the reactions with OH in the stratosphere

$$\log(\tau_{strat}^{OH}) = 1.550 + 0.871 \times \log(\tau_{total}). \quad (11)$$

The lifetime of HFC-143a and methane due to their reactions with OH only in the stratosphere, τ_{strat}^{OH} , follows the same trend as all other HFCs, which can be described by expression (11). The model-derived total stratospheric lifetime of HFC-143a due to both its reactions with OH and O(¹D) is noticeably shorter than

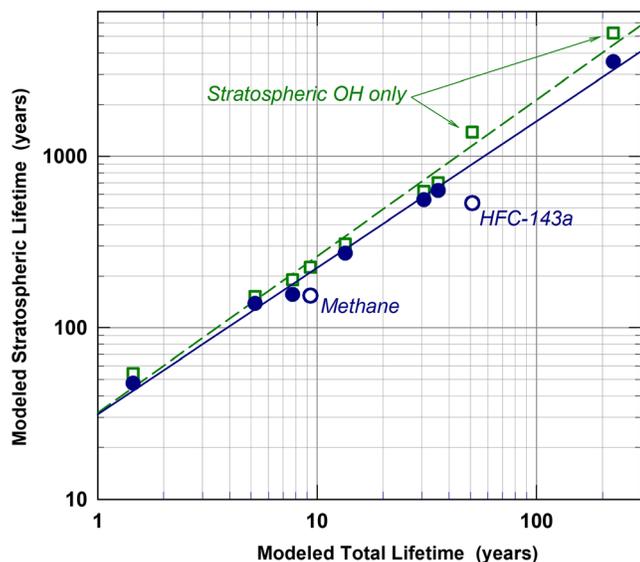


Figure 2. Model-calculated (GSFC2D) partial lifetimes of HFCs due to their reactions in the stratosphere versus total atmospheric lifetimes – solid circles (open circles are HFC-143a and methane). Open squares – lifetimes due to OH reactions only in the stratosphere.

Figure 1 illustrates the persistence of several such HFCs in the stratosphere where they can react with $O(^1D)$. Figure 3 shows partial stratospheric lifetimes due to reactions with $O(^1D)$ calculated with a single model for the longest-lived HFCs versus the rate constants of their $O(^1D)$ reactions (Burkholder et al., 2015; Sander et al., 2011). All results shown in Figure 3 were obtained with GSFC2D but two sets of input kinetic data were used. Results obtained with the $O(^1D)$ reaction rate constants recommended in the 2015 JPL evaluation (Burkholder et al., 2015) and SPARC (2013) are shown as solid circles (solid regression line) whereas those obtained with the earlier 2010 JPL recommendations (Sander et al., 2011) are shown as open circles (dashed regression line). A combined fit to the entire data set yields the following dependence:

$$\log(\tau_{strat}^{O(^1D)}) = -6.457 - 0.9159 \times \log(k_{O(^1D)}) \quad (12)$$

Note that only the reactive channel of the $O(^1D)$ removal rate results in the loss of an HFC molecule. This should not be confused with the total rate constants for $O(^1D)$ removal, which are also reported in Sander et al. (2011) and Burkholder et al. (2015) and include the physical non-reactive quenching of electronically excited $O(^1D)$.

2.2. Stratospheric Photolysis Loss Rates

Photolysis by solar UV radiation near 200 nm in the lower stratosphere is a major loss process for many Cl- and Br-containing hydrocarbons. An empirical dependence between lifetimes of such compounds and their integrated absorption between 200 and 210 nm was suggested and derived in an earlier paper (Orkin et al., 2013) using the total atmospheric lifetimes of CFCs adopted in WMO (2011). Although the choice of wavelength interval for integrating a compounds' absorption cross sections is arbitrary to some extent, 200–210 nm corresponds to the spectral interval where solar UV radiation penetrates to the lower stratosphere. Choosing this interval also results in the same linear dependence among compounds with very different shapes of their UV absorption spectra near

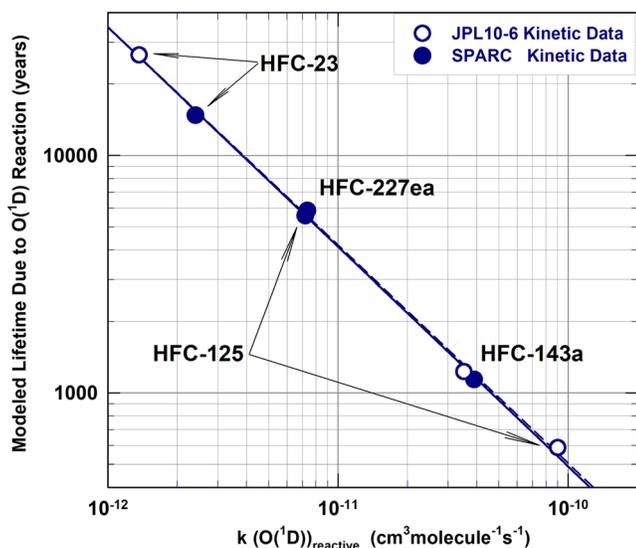


Figure 3. Model-calculated (GSFC2D) partial lifetimes of longer-lived HFCs due to their reactions with $O(^1D)$ only in the stratosphere versus the rate constants of these reactions. The rate constant data are from Burkholder et al. (2015) (closed circles) and Sander et al. (2011) (open circles), respectively.

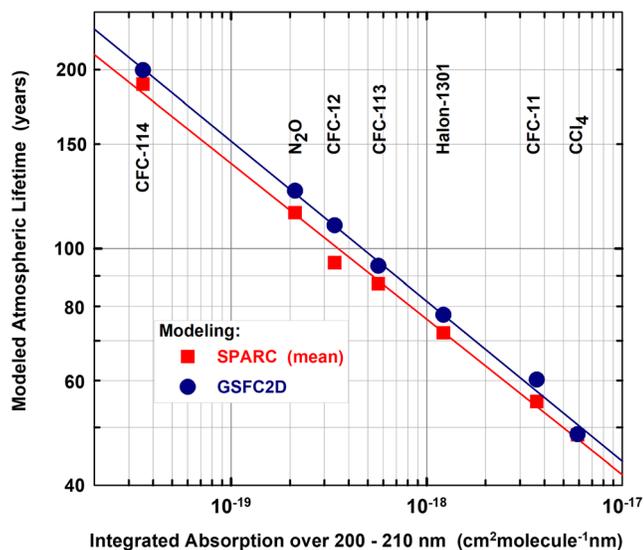


Figure 4. Model-calculated atmospheric lifetimes of CFCs, CCl_4 , Halon-1301, and N_2O versus their UV absorption cross-sections integrated over 200–210 nm: GSFC2D (circles) and the average over seven models used in SPARC (squares).

200 nm, such as CF_3Br and CFCs (see below). In the present paper we derive an updated dependence based on results of the SPARC Report, which were reported in detail in a subsequent paper (Chipperfield et al., 2014). These results showed that although lifetimes of long-lived compounds (e.g., CCl_4 , CFC-11, Halon-1301, CFC-113, and CFC-12) showed similar trends within the same model, their absolute values varied by as much as 20% to 30% among the seven models used. More consistent results for our analysis can be obtained by using only a single model, although results can be biased due to the model chosen. Figure 4 shows the dependences obtained using model average lifetimes from SPARC (2013) and Chipperfield et al. (2014) and using those obtained with GSFC2D (the only model used to study all of the compounds included in the SPARC Report).

For fully halogenated compounds containing at least two Cl-atoms or a Br-atom in the methyl group (e.g., CCl_4 , CFCl_3 , $\text{CF}_2\text{ClCFCl}_2$, CF_2Cl_2 , CF_3Br) photolysis is the major loss process and dictates their atmospheric lifetimes with contribution from reactions with $\text{O}(^1\text{D})$ being as small as 0.7% and 1.8% for Halon-1301 and CFC-11, respectively. This contribution increases to 5.8% in the case of weaker absorbing and, therefore, longer-lived CFC-113 and CFC-12. Reactions with $\text{O}(^1\text{D})$ become even more important for more weakly absorbing compounds with a single

Cl-atom, accounting for 28% of the CFC-114 ($\text{CF}_2\text{ClCF}_2\text{Cl}$) removal rate and at least 40% in case of CFC-115 ($\text{CF}_3\text{CF}_2\text{Cl}$) (Chipperfield et al., 2014; SPARC, 2013).

Results from the SPARC study also indicate a small contribution due to photolysis in the troposphere, which occurs at wavelengths longer than about 290 nm, since radiation near 200 nm has limited penetration into the troposphere and cannot affect a compound's total lifetime. Although there is no strong correlation between tropospheric photolysis and absorption near 200 nm, all Cl-containing compounds exhibit similar UV absorption bands with maxima below 200 nm and gradually decreasing absorption at longer wavelengths (Burkholder et al., 2015). Thus, a stronger absorption near 200 nm can be indicative of stronger absorption at the long wavelength tails above 280–290 nm, which may contribute to tropospheric loss. In any case, this contribution is very small ranging from ~4% and ~3% in case of strong absorbers, CCl_4 and CFCl_3 (CFC-11), respectively, to ~1% in case of weaker absorbers with two Cl-atoms per carbon, CFC-12 and CFC-113 (Chipperfield et al., 2014).

Fits to the data presented in Figure 4 yield

$$\text{GSFC2D model: } \log(\tau_{ph}) = -2.938 - 0.2694 \times \log(\sigma_{200-210}), \quad (13)$$

$$\text{SPARC mean: } \log(\tau_{ph}) = -2.831 + 0.2618 \times \log(\sigma_{200-210}), \quad (14)$$

where $\sigma_{200-210}$ is the integrated absorbance between 200 and 210 nm:

$$\sigma_{200-210} = \int_{200\text{nm}}^{210\text{nm}} \sigma(\lambda) d\lambda$$

$\sigma(\lambda)$, $\text{cm}^2\text{molecule}^{-1}$ is the room temperature absorption cross-section at the wavelength λ , nm.

Dependence (13) was derived from the results obtained for seven stronger UV absorbers whose integrated absorbance exceeds $10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \text{ nm}$. The deviation of results obtained with the same model, GSFC2D, from the expression (13) does not exceed 5% thus suggesting that such correlation can be used to estimate the stratospheric lifetime due to photolysis even when small contributions from $\text{O}(^1\text{D})$ reactions exist. However, it does not work for substantially weaker absorbers, CFC-115 and CFC-13, whose integrated absorption over 200–210 nm is 15–40 times smaller than that of CFC-114 and reactions with $\text{O}(^1\text{D})$ dominate to dictate their lifetimes.

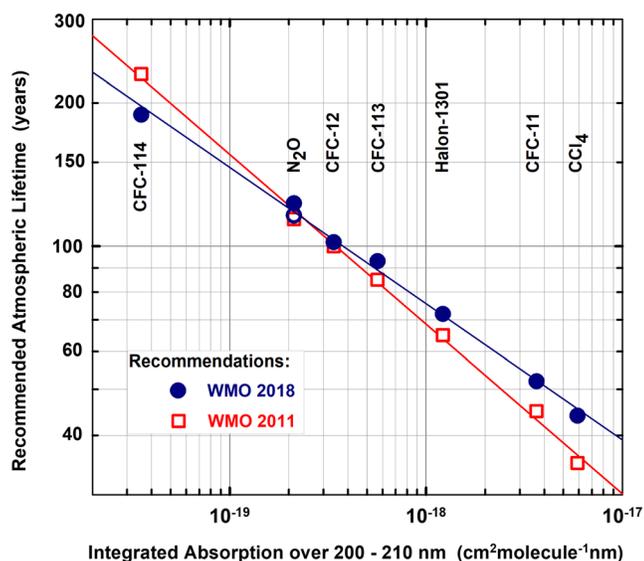


Figure 5. Recommended atmospheric lifetimes of CFCs, CCl₄, Halon-1301, and N₂O versus their UV absorption cross-sections integrated over 200–210 nm: Recommended lifetimes are from WMO (2018) (filled circles) and WMO (2011) (open squares). The updated lifetime of N₂O derived by Prather et al. (2015) is shown with the open circle.

In addition to the model-derived lifetimes, the SPARC Report also included lifetimes inferred from observed trace gases atmospheric distributions (SPARC, 2013). The combination of both model-derived and field measurement-based lifetimes resulted in the recommended values in the SPARC Report, which are slightly different from the modeling results alone (SPARC, 2013). The SPARC recommended values have been incorporated into the WMO (2018) Ozone Assessment. Although these recommended lifetimes are evaluated values rather than lifetimes based solely on modeling of stratospheric photochemical processes with input UV absorption spectra, a dependence similar to (14) can be derived. We also included SPARC recommended lifetimes for nitrous oxide (N₂O) and CFC-114 in the fit to derive the following expression for the

$$\text{WMO(2018)Data: } \log(\tau_{\text{strat}}) = -3.279 - 0.2865 \times \log(\sigma_{200-210}). \quad (15)$$

The deviation of data points from the fitted (WMO, 2018) line shown in Figure 5 is less than 5%. Note that the SPARC (2013) recommended N₂O lifetime is 123 years (with a 1 sigma range of 113–148 years), whereas the more recent comprehensive study by Prather et al. (2015) indicates a slightly shorter atmospheric lifetime of 116 years (with a 1 sigma range of 109–125 years). This newer recommendation is also shown in Figure 5. Using this new $\tau_{\text{N}_2\text{O}}$ in deriving expression (15) results in less than 1% difference in the estimated lifetimes. This can be used for future evaluations, as more accurate data for CFCs lifetimes become available.

Also shown in Figure 5 are the lifetimes from WMO (2011). As can be seen, although the recommended values for CFC lifetimes have been changed since WMO (2011), a linear dependence of $\log(\tau_{\text{strat}})$ versus $\log(\sigma_{200-210})$ exists for both data sets.

$$\text{WMO (2011) Data: } \log(\tau_{\text{strat}}) = -4.591 - 0.3570 \times \log(\sigma_{200-210}). \quad (16)$$

Although these stratospheric removal rates (photolysis lifetimes) include small contributions from reactions with O(¹D) and tropospheric photolysis at longer wavelengths, they are equally well described by the linear dependence between stratospheric removal rate and integrated absorption between 200 and 210 nm and therefore can be used for estimating stratospheric photolysis lifetimes based only on the measured UV absorption spectra of a compound in the absence of modeling results. Since the stratospheric lifetime estimated from the semiempirical dependence (15) is tied to the currently accepted stratospheric lifetimes, this expression can be used to estimate partial lifetimes due to stratospheric photolysis for compounds with strong absorption near 200 nm. This is similar to the use of Equation 10 for estimating partial lifetimes due to chemical reactions in the stratosphere. Thus, these simple relationships provide estimations of partial stratospheric lifetimes of other UV absorbing compounds (such as HCFCs and Br-containing hydrofluorocarbons) and can be useful for quick estimation of active chlorine and bromine loading in the stratosphere due to the compounds' emission at the surface.

2.3. Removal Processes in the Slow Vertical Mixing Stratosphere

Due to fast mixing in the troposphere, reaction with OH and photolysis in the troposphere can be considered as independent processes acting on the same bulk amount of a compound so that their rates can be summed

$$(\tau_{\text{trop}})^{-1} = (\tau_{\text{trop}}^{\text{OH}})^{-1} + (\tau_{\text{trop}}^{\text{phot}})^{-1}. \quad (17)$$

Such combination of removal rates also works when processes occur in two different volumes and, therefore, do not compete with each other and do not influence each other, such as removal processes that occur in the troposphere and stratosphere only. In such cases, the total lifetime of the combined amount of a compound can be expressed as

Table 1
Partial Lifetimes due to Chemical Reactions in the Stratosphere for Chloro-, Dichloro-, and Trichloro-Compounds Estimated From Equation 10 and Obtained by the GSFC2D Model

Compound	Molecule	Estimated partial lifetimes		Model-derived partial lifetimes	
		τ_{strat}^{ph} from (13)	τ_{strat}^m from (10)	τ_{strat}^m GSFC2D	τ_{strat}^{total} GSFC2D
HCFC-22	CHF ₂ Cl	480	233	234	219
HCFC-141b	CH ₃ CFCl ₂	88	181	586	84
MCF	CH ₃ CCl ₃	53	106	737	53

$$(\tau^{total})^{-1} = (\tau_{strat}^{total})^{-1} + (\tau_{trop}^{total})^{-1}. \quad (18)$$

In contrast, removal processes occurring in the “slow vertical mixing” stratosphere can compete with one another by changing the altitudinal distribution of a compound, and the two estimates of partial removal rates due to these stratospheric processes, $(\tau_{strat}^m)^{-1}$ and $(\tau_{strat}^{ph})^{-1}$, should not be combined to get the total stratospheric lifetime, i.e., the following equation,

$$(\tau_{strat}^{total})^{-1} = (\tau_{strat}^{OH})^{-1} + (\tau_{strat}^{ph})^{-1} + (\tau_{strat}^{O(^1D)})^{-1} = (\tau_{strat}^m)^{-1} + (\tau_{strat}^{ph})^{-1}, \quad (19)$$

is not correct in the slow mixing stratosphere. Whereas the OH altitudinal distribution is relatively uniform, the intensity of the incident solar UV radiation near 200 nm increases dramatically with altitude in the lower stratosphere. Therefore, for stronger UV-absorbing HCFCs, photolysis in the slow vertical mixing stratosphere prevents their penetration to higher altitude and thus affects (decreases) the colocated removal rates due to reactions with stratospheric OH and O(¹D), the latter also occurring in the upper stratosphere, i.e.,

$$(\tau_{strat}^{total})^{-1} < (\tau_{strat}^m)^{-1} + (\tau_{strat}^{ph})^{-1}. \quad (20)$$

Thus, expression (19) can only provide a reasonable description of the stratospheric removal rates for compounds having very low UV absorption, which does not disturb their altitudinal distribution. When τ_{strat}^{ph} becomes shorter than τ_{strat}^m , stratospheric photolysis dominates the total removal process by limiting the abundance of the compound in the upper stratosphere, where it could react with OH radicals. Thus, the relative role of photolysis as the stratospheric removal process can actually be larger than one might first think based only on the ratio of τ_{strat}^m (which is estimated in the absence of photolysis) to τ_{strat}^{ph} (which is estimated in the absence of reactions). Table 1 illustrates this by presenting the stratospheric lifetime due to chemical reactions estimated from (10) and those partial lifetimes obtained with the GSFC2D model. One can see that these values are the same for the low UV-absorbing HCFC-22 (CHF₂Cl) containing only a single Cl atom. The discrepancy appears and increases with increasing UV absorption for compounds containing dichloro- and trichloro-methyl groups. In the case of strong absorbers such as MCF and HCFC-141b ($\tau_{strat}^{ph} < \tau_{strat}^m$) the modeled stratospheric lifetime is actually closer to the estimated stratospheric photolysis lifetime, τ_{strat}^{ph} . The situation becomes more complicated and the results are not so obvious without modeling in the case of weaker absorbers or fast OH reactions when photolysis and reactive loss in the stratosphere are comparable loss processes.

A similar situation occurs in the case of non-UV absorbing HFCs due to the competition between the OH and O(¹D) reactive losses in the slow vertical mixing environment of the stratosphere. Compounds with faster OH reactions have shorter total lifetimes and modified altitudinal distributions in the stratosphere. When a compounds' local OH removal rate in the lower stratosphere exceeds the rate of vertical mixing, significant concentrations do not reach the upper stratosphere where the O(¹D) reactive loss is important. This decreases the possible influence of the O(¹D) reaction on the lifetime, so that

$$(\tau_{strat}^{total})^{-1} < (\tau_{strat}^{OH})^{-1} + (\tau_{strat}^{O(^1D)})^{-1}. \quad (21)$$

Table 2
Partial Lifetimes due to Reactions With O(¹D) and Total Lifetimes of Non-UV-Absorbing Compounds Estimated From Equation 12 and Obtained by the GSFC2D Model

Compound	Molecule	τ_{total} , years	$\tau_{strat}^{O(^1D)}$, years	
			Equation 12	GSFC2D
HFC-23	CHF ₃	223.8	15,331	14,806
HFC-143a	CH ₃ CF ₃	50.98	1,193	1,138
HFC-125	CHF ₂ CF ₃	30.65	5,500	5,860
Methane	CH ₄	9.32	302	496
HFC-245fa	CHF ₂ CH ₂ CF ₃	7.73	655	1,007
HFC-32	CH ₂ F ₂	5.2	2,810	5,381
HFC-152a	CH ₃ CHF ₂	1.45	521	2,659

Table 2 illustrates the decreasing role of the O(¹D) reaction for shorter-lived nonabsorbing compounds. The fourth column shows lifetimes due to reactions with O(¹D) estimated from the dependence (12), i.e., obtained by assuming minimal influence of fast OH reactions in the lower stratosphere. The next column shows the same partial lifetimes due to O(¹D) reactions calculated with GSFC2D model, i.e., in the presence of OH reactions in the lower stratosphere, which limit the access of compounds to higher altitudes to react with O(¹D). The total lifetime of compounds due to their reactions with OH are shown in the third column as a measure of a compounds' reactivity with OH. One can see that expression (12) noticeably underestimates the partial lifetimes of shorter-lived compounds (i.e., overestimates partial removal rates) due to their reactions with O(¹D) in the slow mixing stratosphere.

3. Tropospheric and Total Lifetimes (Estimating Total Lifetimes)

With simple analytical expressions for partial lifetimes derived above from GSFC2D atmospheric model results, we can constrain the estimation of a compound's total lifetime and compare the results with those calculated from the same GSFC2D model. All results presented in Figures 6–8 are the differences between the estimated lifetimes and the corresponding model-derived values.

First, we calculated scaled lifetimes by using the expression (4), which is widely used to estimate the lifetimes due to reactions with OH radicals in the troposphere only.

$$\tau_{RH_i}^{OH} = \frac{k_{MCF}(272\text{ K})}{k_{RH_i}(272\text{ K})} \cdot \tau_{MCF}^{OH}$$

These results are shown in Figure 6, which illustrates that expression (4) underestimates the tropospheric lifetime of a compound. This is apparently due to the noticeable additional reservoir of the longer-lived compounds in the stratosphere (see Equation 9 and Figure 1), which is not accounted for when using expression (4) but does affect results of more rigorous model calculations. There are three obvious outliers, methyl bromide (CH₃Br), HCFC-141b (CH₃CFCl₂), and MCF (CH₃CCl₃). These compounds are strong UV absorbers and their abundance in the stratosphere is very limited due to fast photolysis in the lower stratosphere. Thus, their global atmospheric reservoir is similar to their abundance in the troposphere and the expression (4) yields more accurate values for their tropospheric lifetimes, i.e., $\tau_{RH_i}^{OH} \approx \tau_{trop}^{OH}$

for such compounds. Thus, the first major conclusion from this work is that the MCF scaling approach given by expression (4) is not the most accurate way for estimating a compound's tropospheric lifetime.

Prather et al. (2012) suggested correcting $\tau_{RH_i}^{OH}$ with “atmospheric fill factors” for each gas, which are based on observed profiles to account for the fall-off in abundance through the stratosphere. Thus, the corrected partial lifetimes due to reactions with OH in the troposphere can be derived, which corresponds to the first summand in expression (9). However, the second summand in expression (9) representing the partial lifetime due to stratospheric removal processes remains unknown. Also, stratospheric concentration profiles required for calculating corrective “fill factors” are not available for new chemicals.

Second, we calculated the total lifetimes, τ_{total} , by combining all estimated local removal rates due to reactions with OH in the troposphere (4), reactions with OH and O(¹D) in the stratosphere (10), and the stratospheric photolysis (13)

$$(\tau_{total})^{-1} = \left(\tau_{RH_i}^{OH}\right)^{-1} + \left(\tau_{strat}^{ns}\right)^{-1} + \left(\tau_{strat}^{ph}\right)^{-1} \quad (22)$$

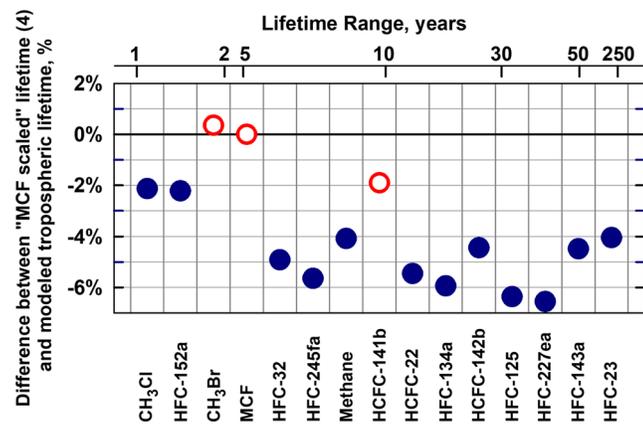


Figure 6. Differences (%) between “methyl chloroform scaled” lifetimes calculated from (4), $\tau_{RH_i}^{OH}$, and GSFC2D model-calculated partial lifetimes due to OH reactions in the troposphere only. Open circles indicate strongest UV absorbers, CH₃Br, CH₃CCl₃, and CH₃CFCl₂.

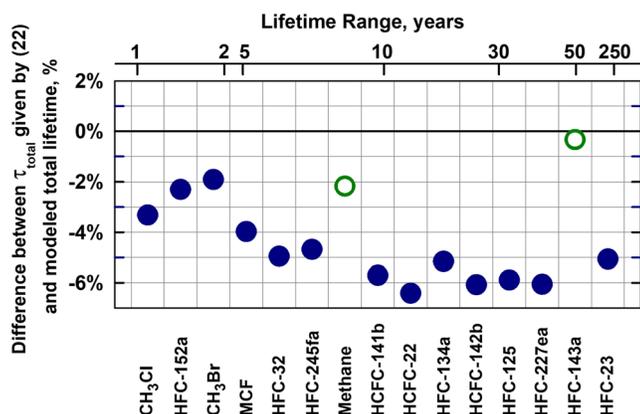


Figure 7. Differences (%) between “methyl chloroform scaled” lifetimes, $\tau_{RH_i}^{OH}$, corrected with total stratospheric reaction lifetimes and photolysis lifetime (22) and GSFC2D model-calculated total lifetimes of compounds. Open circles indicate CH_3 -containing compounds, which do not absorb UV radiation, CH_4 and CH_3CF_3 .

between $\tau_{RH_i}^{OH}$ obtained from the scaling procedure (4) alone and the GSFC2D model-calculated total lifetimes. Open squares denote Br-, Cl-containing compounds, which can absorb the UV radiation in the stratosphere, whereas open circles denote nonabsorbing compounds (HFCs and methane).

Obviously, significant corrections should be made to account for UV absorption. We combined corresponding lifetimes, obtained from (4) and (13) to derive the total lifetimes of UV absorbing compounds:

$$(\tau_{total})^{-1} = (\tau_{RH_i}^{OH})^{-1} + (\tau_{strat}^{ph})^{-1}. \quad (23)$$

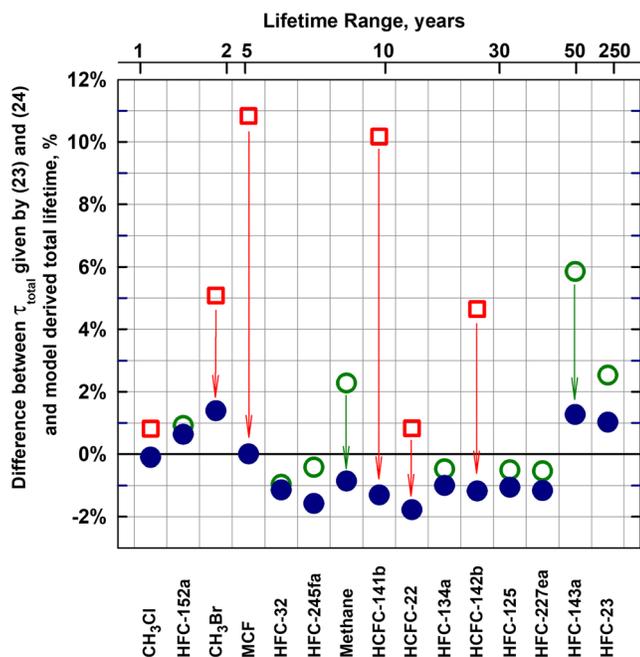


Figure 8. Differences (%) between estimated and GSFC2D model-calculated total lifetimes of compounds. “Methyl chloroform scaled” lifetimes, $\tau_{RH_i}^{OH}$, are shown with open squares (HCFCs and CH_3Br) and open circles (HFCs and methane). Solid circles show these data after adjustment for either photolysis in the stratosphere (23) or reactions with $\text{O}(^1\text{D})$ in the stratosphere (24), respectively.

Such an approach has often been used for estimating the total lifetime of a compound in the atmosphere (WMO, 2011, 2018). Results are shown in Figure 7, which illustrates that expression (22) underestimates the total lifetime of a compound. The two largest outliers, methane (CH_4) and HFC-143a (CH_3CF_3), both contain a nonsubstituted methyl group ($-\text{CH}_3$), which is very reactive toward $\text{O}(^1\text{D})$ as discussed earlier (section 2.1) and shown in Figure 2. We suggest that this discrepancy is due to an overestimation of the stratospheric removal rate, which is mainly due to stratospheric OH reactions, expression (11). Therefore, the second significant conclusion from this work is that the simple combination of $\tau_{RH_i}^{OH}$ estimated from expression (4) with estimated stratospheric OH and $\text{O}(^1\text{D})$ reaction and photolysis rates, expression (22), underestimates a compound's total atmospheric lifetime.

Finally, we have examined adding only loss rates due to stratospheric photolysis (13) and reactions with $\text{O}(^1\text{D})$ in the stratosphere (12) to $(\tau_{RH_i}^{OH})^{-1}$ estimated from (4). Figure 8 presents the results of this approach and clearly illustrates the role of stratospheric photolysis and reactions with $\text{O}(^1\text{D})$. Open symbols (both circles and squares) are differences

The results are shown with the corresponding solid circles in Figure 8. Note that τ_{strat}^{ph} calculated with expression (13) actually takes care of some input from reactions of $\text{O}(^1\text{D})$ with low UV-absorbing compounds as expression (13) was derived as the correlation between the total lifetime of CFCs and their integrated absorption near 200 nm. Reactions with $\text{O}(^1\text{D})$ are minor sinks for stronger absorbing compounds with more than one Cl atom in the methyl group.

In the case of nonabsorbing compounds, the noticeable difference with model-calculated lifetimes appears only for HFC-143a and methane. The higher reactivity of these compounds with $\text{O}(^1\text{D})$ has been discussed earlier. However, we used $\tau_{strat}^{O(^1D)}$ derived from (12) to estimate the total lifetimes of all nonabsorbing compounds:

$$(\tau_{total})^{-1} = (\tau_{RH_i}^{OH})^{-1} + (\tau_{strat}^{O(^1D)})^{-1}. \quad (24)$$

The results are shown with the corresponding solid circles in Figure 8. Thus, the accurate estimation of the total lifetime of a compound in the atmosphere can be made by combining the scaled tropospheric lifetime, $\tau_{RH_i}^{OH}$, derived from (4) with the photolysis lifetime, τ_{strat}^{ph} , derived from (13) for UV absorbing compounds, and with the $\text{O}(^1\text{D})$ reaction lifetime, $\tau_{strat}^{O(^1D)}$, for nonabsorbing compounds.

The modeled contribution of the photolysis in the mesosphere at 121.6 nm Lyman- α wavelength is 1.5% and 0.5% for the longest-lived compounds,

HFC-143a and HFC-23, respectively. Thus, the corresponding points in Figure 8 could be shifted slightly down to be even more consistent with other compounds, whose Lyman- α photolysis makes a negligible contribution to the total lifetime ($<0.1\%$). This process has been omitted from our analysis in the very beginning (expression (3)).

4. Summary

Analysis of the modeling results from SPARC (2013) and, in particular, those performed with the GSFC2D model suggests that very accurate estimates of the total atmospheric lifetimes of halogenated hydrocarbons can be obtained from the MCF scaling method (Prather & Spivakovsky, 1990) with proper adjustments for the other atmospheric loss processes even though the method was proposed for estimating only tropospheric partial lifetimes. The only two needed adjustments are (i) to account for the UV stratospheric photolysis in case of UV absorbing compounds and (ii) to account for reactions with $O(^1D)$ in case of nonabsorbing compounds. In fact, the first correction is essential only for strong UV absorbers containing CCl_3 , CCl_2 , or CBr in the molecule, whereas the second correction is essential mainly for $-CH_3$ containing molecules. These corrections can be made by using expressions (23) or (24), respectively. Note that τ_{strat}^{ph} describes only photolysis in the stratosphere and does not work for compounds with significant absorption of UV radiation above 290 nm penetrating to the troposphere which will shorten the compounds' lifetime.

For use in expression (23), the partial lifetime due to stratospheric photolysis, τ_{strat}^{ph} , can be estimated from expression (15), which is derived from the lifetimes of nonreactive compounds currently recommended based on both atmospheric modeling and field measurements of their abundance and trend. Similarly, for use in expression (24) the partial lifetime due to reactions with $O(^1D)$, τ_{strat}^m , can be estimated from expression (12), which is based on results of a single model, GSFC2D, calculated with the currently recommended kinetic data (Burkholder et al., 2015; Sander et al., 2011).

Expression (15), which is based on the recommended stratospheric photolysis lifetimes given in SPARC, 2013 and WMO, 2018 for CFCs yields $\tau_{MCF}^{ph} = 48$ years for the partial lifetime of methyl chloroform (MCF) due to stratospheric photolysis. This is longer than the value of 38 years reported in WMO, 2018. The value of 38 years can also be obtained from expression (16), which was derived using CFC photolysis lifetimes reported in WMO (2011). This difference is consistent with the change in the recommended lifetime of CFC-11 from 45 years (WMO, 2011) to 52 years (SPARC, 2013; WMO, 2018) since the UV absorption spectra of MCF and CFC-11 are very similar. The total atmospheric lifetime of methyl chloroform currently derived from measurements of its abundance in the atmosphere is $\tau_{MCF}^{total} = 5.04_{-0.29}^{+0.33}$ years (Rigby et al., 2013; SPARC, 2013). This value can be combined with the value of $\tau_{MCF}^{ph} = 48$ years derived above and the estimated lifetime of $\tau_{MCF}^{ocean} = 94_{-13}^{+51}$ due to oceanic loss (Yvon-Lewis & Butler, 2002) to obtain

$$\tau_{MCF}^{OH} = \left[\left(\tau_{MCF}^{total} \right)^{-1} - \left(\tau_{MCF}^{ph} \right)^{-1} - \left(\tau_{MCF}^{ocean} \right)^{-1} \right]^{-1} = 5.99 \text{ years.} \quad (25)$$

The resulting partial lifetime of MCF due to reaction with OH in the troposphere, $\tau_{MCF}^{OH} = 6.0$ years is slightly different from the currently used value of 6.1 years (WMO, 2018).

Montzka et al. (2011) derived a nearly constant exponential decay (decay rate of $0.181 \pm 0.005 \text{ years}^{-1}$) of global MCF abundance from results of the NOAA field measurement network during the period 1998–2007, the decade following a rapid emission decline owing to revised Montreal Protocol guidelines (McCulloch & Midgley, 2001). Holmes et al. (2013) reported similar decay rates derived from results of the NOAA (0.1811 year^{-1}) and AGAGE (0.1796 year^{-1}) networks. If one assumes this observed decay is not affected by any emission, the total lifetime of MCF, τ_{MCF}^{total} , would be estimated to be ≈ 5.5 years, which yields $\tau_{MCF}^{OH} \approx 6.7$ years after correction for the stratospheric photolysis and oceanic loss. However, although the global emission rate of MCF declined after 1990 to become significantly smaller than its global atmospheric oxidation rate, a small sustained emission can noticeably affect the observed atmospheric decay rate. The small emission in the late 1990s reported by McCulloch and Midgley (2001) and Rigby et al. (2017) indicates that there was ongoing release of MCF to the atmosphere, at least through 2014. A simple estimation shows that a continuous global emission rate as small as only $\approx 1\%$ of the global oxidation rate in the beginning of the

10-year observation period can result in a $\approx 10\%$ decrease in the observed exponential decay rate. Thus, the value of 5.5 years can be considered as a possible upper limit of the MCF atmospheric lifetime.

Thus, the total lifetime of a halogenated compound in the atmosphere can be empirically estimated from the following expressions based on results of laboratory measurements of its UV absorption spectrum and reactivity toward hydroxyl radicals (OH) and O(¹D) atoms. The latter is important for long-lived compounds and those containing a -CH₃ group.

$$\tau_{RH_i}^{OH} = \frac{k_{MCF}(272\text{ K})}{k_{RH_i}(272\text{ K})} \times \tau_{MCF}^{OH} = \frac{k_{MCF}(272\text{ K})}{k_{RH_i}(272\text{ K})} \times 6.0, \text{ years} = \frac{3.68 \times 10^{-14}}{k_{RH_i}(272\text{ K})}, \text{ years}$$

$$\text{CFCs:} \quad \log(\tau_{strat}^{ph}) = -3.279 - 0.2865 \times \log(\sigma_{200-210}) \quad (\text{Figure 5})$$

$$\text{HCFCs:} \quad (\tau_{total}^{HCFC})^{-1} = (\tau_{RH_i}^{OH})^{-1} + (\tau_{strat}^{ph})^{-1}$$

$$\text{HFCs:} \quad (\tau_{total}^{HFC})^{-1} = (\tau_{RH_i}^{OH})^{-1} + (\tau_{strat}^{O(^1D)})^{-1}$$

$$\text{where} \quad \log(\tau_{strat}^{O(^1D)}) = -6.457 - 0.9159 \times \log(k_{O(^1D)}) \quad (\text{Figure 3}).$$

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